

## Effect of Ruthenium Oxide/Titanium Mesh Anode Microstructure on Electrooxidation of Pharmaceutical Effluent

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### Abstract

The present contribution investigates the influence of Ruthenium oxide ( $\text{RuO}_2$ ) microstructure on titanium substrate for treatment of pharmaceutical effluent.  $\text{RuO}_2/\text{Ti}$  electrodes were prepared at two different sintering temperatures viz.  $450^\circ\text{C}$  and  $550^\circ\text{C}$ , and subjected to degradation studies on pharmaceutical effluent. Fourier Transform Infrared spectroscopy (FT-IR) was used for analysis of intermediates formed during degradation. The performance of these electrodes were presented and discussed on the basis of sintering temperatures. Electrodes prepared at  $450^\circ\text{C}$  and  $550^\circ\text{C}$  gave 84% and 96% color removal respectively. Chemical Oxygen Demand (COD) removal was found to be 68% and 79% for the electrodes prepared at  $450^\circ\text{C}$  and  $550^\circ\text{C}$  respectively. The surface morphology of these electrodes were identified and studied by Scanning electron Microscopy (SEM). X Ray Diffraction (XRD) patterns showed the presence of anatase phase  $\text{TiO}_2$  at  $550^\circ\text{C}$ . The microstructural changes on sintering the catalytic coating caused a significant improvement in anode performance in electrodes sintered at  $550^\circ\text{C}$ . The electrodes are electrochemically active and stable, and are chemically inert under operating conditions.

**Keywords:** Pharmaceutical effluent;  $\text{RuO}_2/\text{Ti}$  anode; Electro-oxidation; Microstructure; X Ray Diffraction; Scanning Electron Microscopy

### Introduction

Pharmaceutical industries in and around Chennai, India produce a wide variety of products using both organic and inorganic substances as raw materials, thereby generating a large quantity of complex toxic organic liquid wastes with high concentrations of inorganic TDS. These wastes are highly toxic to biological life, and are usually characterized by high BOD, COD and COD: BOD ratio. In addition, wastes from drug manufacture also contain toxic components including cyanide [1]. Ground water quality is disturbed by penetration of pharmaceutical industry effluents. Advanced oxidation processes (AOPs), which rely on the generation of very reactive short lived hydroxyl radicals have been attempted to decontaminate pharmaceutical wastewater. Electro-oxidation is one of the recent techniques which have been used in the treatment of pharmaceutical wastewater in an effective manner [2-5]. Industrial use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological solutions, thus reducing operational and investment costs [6,7]. Such DSA-type materials have been used for the oxidation of model aqueous solutions containing non biodegradable organics, typically found in pharma effluents. Recent DSA research emphasis focuses on titanium based anodes coated with a variety of oxide materials such as  $\text{IrO}_2$ ,  $\text{Ru}_2\text{O}_3$ , and  $\text{SnO}_2$ . DSA with  $\text{RuO}_2\text{-TiO}_2$  coated titanium has been used widely and successfully as anode for chlor-alkali production and electro-oxidation of wastewater due to its good electro catalytic activity.  $\text{RuO}_2$  is a good electro catalyst for oxygen evolution, in spite of limited service life [8]. The coating of  $\text{RuO}_2$  by thermal decomposition of the precursors such as  $\text{RuCl}_3$ , can persist on titanium mesh surfaces for long durations and cause the activation of titanium anode through its pores. Surface activation by  $\text{RuO}_2$  can occur only if the coating is sufficiently porous for diffusion of the ions involved during electro-oxidation. The coating also shows a high pseudo capacitance value due to the redox reactions of  $\text{RuO}_2$ . At  $400^\circ\text{C}$ , the normal firing temperature of  $\text{RuCl}_3$  on titanium substrate, ruthenium penetrates deep into the bulk of the substrate and accumulates in the near surface region. The chemical stability and the electrochemical properties of  $\text{RuO}_2$  layers are strongly dependent on

their preparation process.

The  $\text{Ti}/\text{RuO}_2$  system has received considerable attention due to its excellent stability, electro catalytic properties and prevention of Ti passivation by the oxide coating. A further advantage is the large number of Ru-oxidation states existing at the electrode surface in the potential region between the hydrogen evolution reaction, HER, and the oxygen evolution reaction, OER. The electrochemical oxidation of organic substances was attributed to  $\text{OCl}^-$ ,  $\text{OH}^-$ , nascent oxygen and other reactive [9].

Titanium based anodes are unavoidable in the electro oxidation techniques. This type of anode is mostly coated with catalytic oxides such as Ruthenium oxide or iridium oxide to enhance the oxidation process of the anode [10,11]. The present work has the objective to study the effect of sintering temperature on  $\text{RuO}_2$  coated titanium mesh anodes by means of preparing  $\text{RuO}_2$  coating at two different temperatures. The coated electrodes are then employed for the treatment of pharmaceutical effluents [12-14]. The results obtained elucidate the effect of  $\text{RuO}_2$  microstructural modifications at over Ti substrate at different sintering temperatures  $450^\circ\text{C}$  (Electrode A) and  $550^\circ\text{C}$  (Electrode B) on efficient electro-oxidation performance.

### Materials and Methods

#### Materials

All chemicals employed were of the "AR" grade, and purchased from Merck India Ltd. Calibration of laboratory equipments were carried

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out with due accordance to accepted standards, and double de-ionized water was used while conducting all experiments. The pharmaceutical effluent samples were collected from a private pharmaceutical industry at Chennai, India. Table 1 provides the physico-chemical properties of effluent prior to electro-oxidation.

### Anode fabrication

The anode substrate consisted of commercially available rectangular titanium mesh of 99% purity, with a 5 x 4 x 0.4 cm<sup>3</sup> dimension. RuCl<sub>2</sub>·3H<sub>2</sub>O solution was prepared in isopropanol, and used as the precursor. Post precursor application, the anode surface was dried and fired at two different temperatures, viz. 450°C (electrode A) and 550°C (electrode B) in the presence of air for a period of 10 min [15-17]. Surface pre-treatment of titanium substrate prior to RuO<sub>2</sub> coating was seen to be critical for the fabrication of stable electrodes. Etching of the substrate was done in HCl solution at 70°C for a 1-2 min time duration.

### Electro oxidation procedure

About 200 ml of the effluent was taken in an electrochemical reactor. The anode was a catalytically coated titanium electrode and the cathode was a thin plate of stainless steel. The two electrodes were separated by a distance of about 2 cm. A current density of about 3 A/dm<sup>2</sup> was supplied between the electrodes. The sample to be analysed was pipetted out once in every one hour. The whole process was carried for 4 hours. The same experiment was carried out with both the electrodes electrode A and electrode B.

### Physico-chemical characterization

The surface morphology of RuO<sub>2</sub> coatings at different temperatures was characterized using SEM (Bruker TESCAN) prior to and post electro-oxidation at 3 A/dm<sup>2</sup> for 4 hr. The coating from anodes A and B were scraped from the anode surface and ground well. The powder so obtained was used to determine the crystalline characteristics of the metal oxides by X-ray diffraction (XRD) analysis.

### Electrochemical measurements

The electrochemical behaviour of RuO<sub>2</sub>/Ti mesh anodes A and B prepared at two different temperatures were studied by cyclic voltmmetry. The anode mesh under study was employed as the working electrode, with an exposure area of 1 cm<sup>2</sup> in pharmaceutical effluent solution containing 1 g/L NaCl as supporting electrolyte. Saturated Calomel Electrode (SCE) and stainless steel were used as the reference electrode, and counter electrodes respectively. The cyclic voltammograms were recorded by sweeping the potential (Vs SCE) across the range of -0.8 to +1.2 V at a 5 mV/s scan rate. Studies were performed using a BIOLOGIC electrochemical analyzer.

### COD Measurements

Measurements of COD in the pharmaceutical effluent were made at regular time intervals by acid solution precipitation method, as reported in our previous contribution [18]. COD acid and Potassium Dichromate

S. no.	Parameter	Raw effluent
1	Color	Dark brown
2	pH	8.1
3	COD	1572 mg/l
4	BOD	965 mg/l
5	Total dissolved solids	215 mg/l

Table 1: Physico-chemical characteristics of raw pharmaceutical effluent.

solutions were mixed with a pre-determined quantity of effluent solution. The mixture was placed in a COD digester (Spectroquant TR 420, Merck) at 148°C for 120 min. It was then titrated against ferrous ammonium sulphate (FAS) solution using Ferrohin as the indicator. A change in color from red to brown indicated the end point. The COD was then calculated by the formula previously reported [18].

## Results and Discussion

### SEM observation

SEM observations were carried out for viewing variations in the morphology and structure of the two types of mesh catalyst coatings prepared at 450°C (Electrode A) and 550°C (Electrode B). Figs. 1 and 2 the SEM micrographs of the RuO<sub>2</sub> coated titanium electrodes prepared by conventional thermal decomposition procedure (Electrode A) prior to and post electro-oxidation at 3 A/dm<sup>2</sup> for 4 hr. Dried-mud cracks can be found in flat areas for both oxide electrodes, which is very typical for DSA type electrodes as a result of sintering process. A number of crystallite agglomerates are seen on the surface of electrode A. Some of the precipitates scatter in the flat area, while others are seen to be distributed along the ridges. This morphology with dried-mud cracks, flat areas and agglomerates is typical for RuO<sub>2</sub> coated titanium electrode derived from conventional thermal decomposition, as reported in previous literature [19].

The SEM images of electrodes prepared at 550°C (Electrode B) prior to and post electro-oxidation are provided in the Figures 3 and 4. It can be seen from these images that the size of RuO<sub>2</sub> oxide grains in the electrode B is much lower than that of electrode A. The agglomeration of crystallites is also found to be minimal in comparison to that of electrode A. This may be attributed to the formation of stable anatase phase RuO<sub>2</sub> on sintering at 550°C, resulting in the formation of small particles with high surface area, which is most suitable for electro catalytic oxidation process. There are number of pores on the surface of electrode B, contributing to the increased catalytic property and more reactive surfaces. This micro structural variation in electrode B contributes to more efficient treatment of pharmaceutical wastewater,

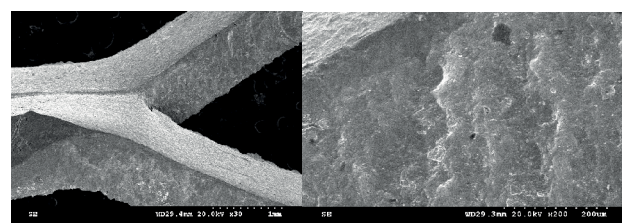


Figure 1: SEM image of RuO<sub>2</sub>/Ti electrodes sintered at 450°C (Electrode A) prior to electrooxidation.

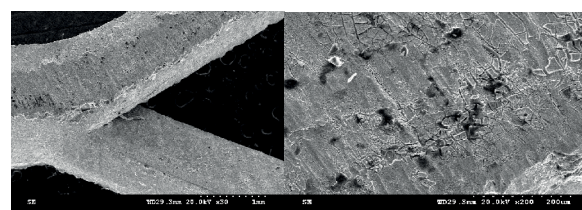


Figure 2: SEM image of RuO<sub>2</sub>/Ti electrodes sintered at 450°C (Electrode A) post electro-oxidation at 3 A/dm<sup>2</sup> for 4 hr.

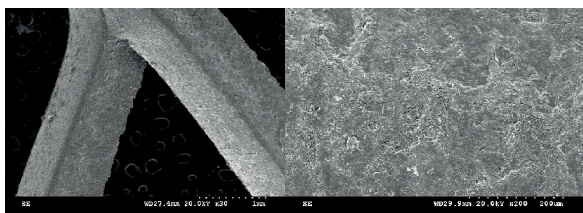


Figure 3: SEM image of RuO<sub>2</sub>/Ti electrodes sintered at 550 °C (Electrode B) prior to electrooxidation.

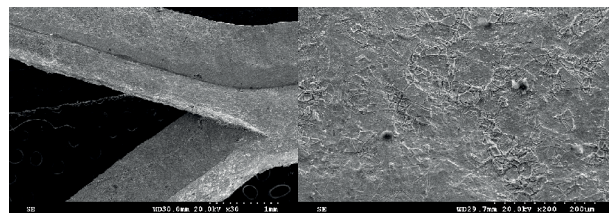


Figure 4: SEM image of RuO<sub>2</sub>/Ti electrodes sintered at 550 °C (Electrode B) post electro-oxidation at 3 A/dm<sup>2</sup> for 4 hr.

as depicted by further results presented in this report. The cracks that are formed on the surface of the electrode after electro-oxidation may be due to the evolution of chlorine gas and the evaporation of water vapor [20-25]. As observed from the Figures 2 and 4, the SEM images of electrodes A and B post electro-oxidation; it is evident that the electrode B is more stable than that of electrode A under operating conditions.

### XRD analysis

XRD analysis was collected to help further characterize the coatings and highlight areas of similarity and difference between thermally decomposed electrodes prepared each at electrode A and at electrode B. The diffraction peaks were indexed in accordance to the standard data provided by JCPDS. Figure 5 (a) and 5(b) are the XRD patterns of RuO<sub>2</sub>/Ti anodes prepared at 450°C (Electrode A) and 550°C electrode B. Diffraction peaks were observed at 25.32°, 37.56°, and 56.45°, corresponding to the anatase phase of RuO<sub>2</sub>. The intensity of RuO<sub>2</sub> anatase diffraction peaks was seen to be higher in electrode B when compared to that of electrode A, which is an indication that the crystalline nature of anatase RuO<sub>2</sub> increases with increasing sintering temperature. This is illustrated by smaller sized grains and RuO<sub>2</sub> refined microstructure on the surface as electrode B, as illustrated by the SEM images. The porous surface nature results in an increased number of active sites, improving the electrocatalytic activity of electrode B for pharmaceutical effluent electro-oxidation. This is well revealed by results from COD removal and FT-IR studies. It is also important to mention here that the rutile phase of RuO<sub>2</sub> begins to form on sintering above temperatures of 600°C.

### Cyclic voltammetry studies

Cyclic voltammetry studies (Figure 6) were carried out in order to compare the electrochemical stability of electrodes prepared at two different temperatures. The oxidation and reduction of pharmaceuticals in electrode B were found to occur at -0.45 V and 0.15 V respectively. It can be observed that durability of electrode B is much higher than electrode A. The difference in stability could be related to micro structural characteristics of the oxides in the coating. The oxides in electrode B are present in smaller crystallite sizes, resulting in enhanced cohesion between formed particles, and contribute to improvement in stability. Though it is a fact that stability could be altered by morphological and micro structural properties of the films, one has to take into account the effect of the real current density, i.e., the current normalised by the real surface area. In this sense, the real current density for the electrodes prepared at electrode A is lower which has lesser surface area as clearly indicated in Figure 6. Therefore, changing the preparation method could be considered as an approach to improve material performance. The SEM images showed that the RuO<sub>2</sub> films were totally damaged after electro-oxidation using electrode A (Figure 2).

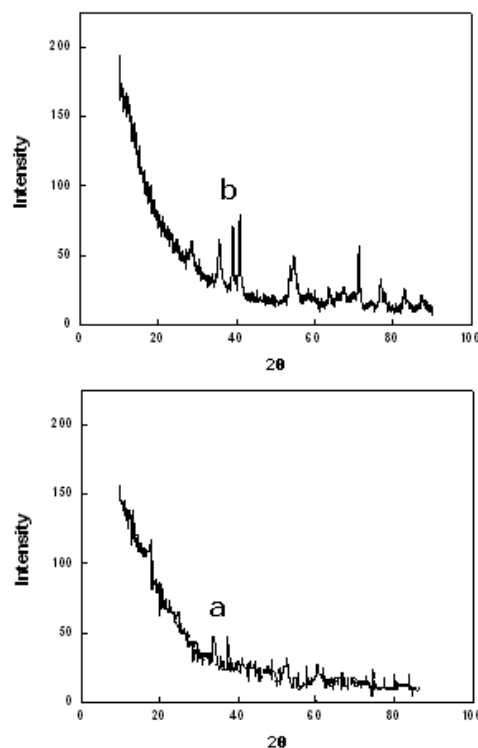
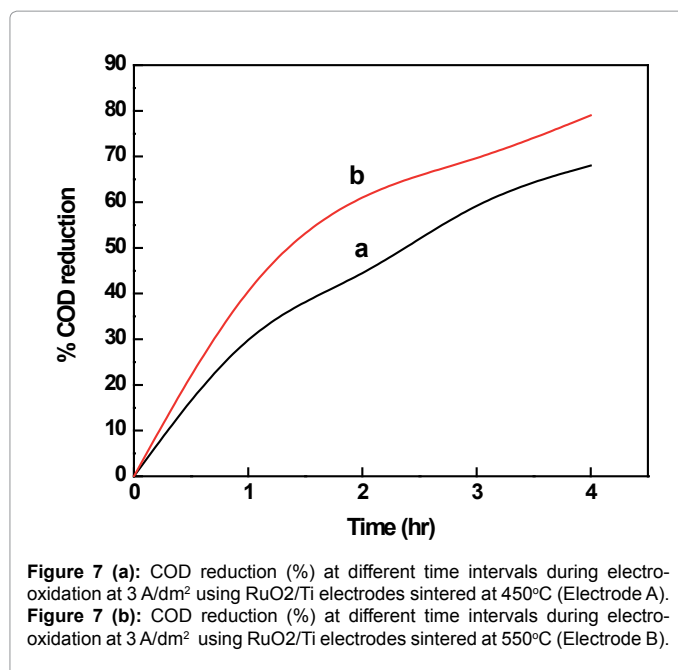
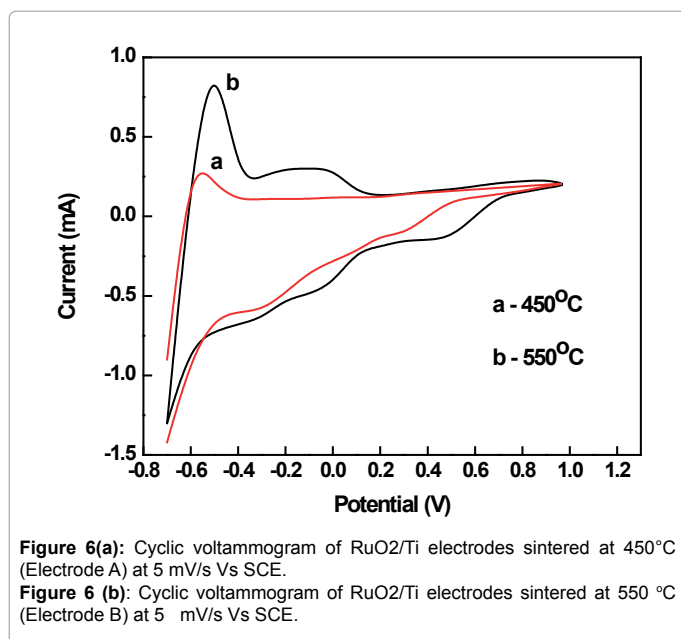


Figure 5 (a): XRD pattern of RuO<sub>2</sub>/Ti electrodes sintered at 450°C (Electrode A) prior to electrooxidation.

Figure 5 (b): XRD pattern of RuO<sub>2</sub>/Ti electrodes sintered at 550 °C (Electrode B) prior to electrooxidation

Therefore, dissolution of the RuO<sub>2</sub> occurs, which is associated with the formation of unstable ruthenium species, such as Ru(VI) and Ru(VIII) at this temperature. Erythromycin and amoxicillin undergoes oxidation at the peak potential of background response which indicates that erythromycin and amoxicillin is indirectly oxidized by some reactive species in the background electrolyte. This suggests that the oxidation of pharmaceuticals occur through indirect oxidation by hydroxyl or other oxidant reagent electro generated from the supporting electrolyte (mainly OCl<sup>-</sup> ions in NaCl). Among all the results, the redox behavior and intensity of oxidation/reduction peaks was more pronounced in electrode B than that of electrode A. This observation can be attributed to high active surface area of the electrode B, which is rendered by smaller crystallite sizes and microstructural modifications occurring during sintering of electrodes at 550°C used in this study. The feasibility of electrode B for the electrochemical oxidation of pharmaceuticals is indicated by voltammetric observations.



### Electrode performance

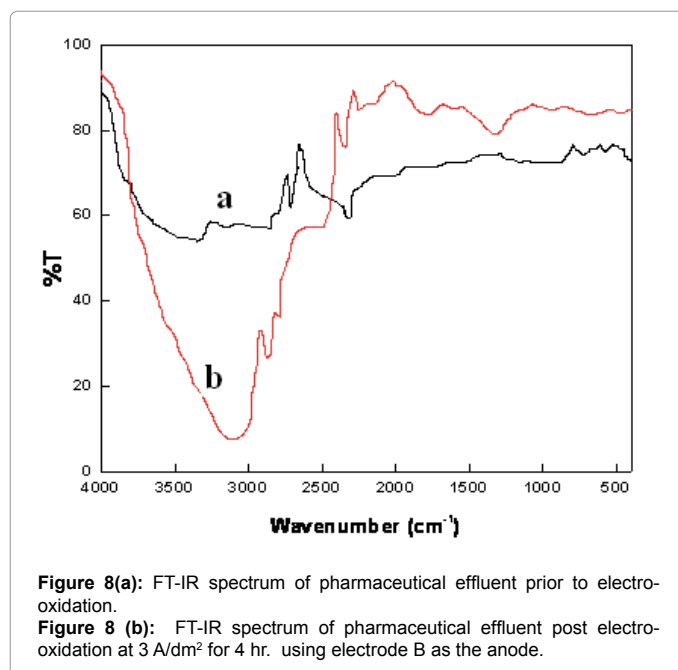
Reduction in Chemical Oxygen Demand (COD) of the pharmaceutical effluent during electro-oxidation at a constant current density of 3 A/dm<sup>2</sup> was monitored at different time durations, and the results are provided in Figure 7. The rate of COD removal during the initial stages of the electrooxidation was observed to be high especially in anodes prepared at electrode B. Decrease in rate of COD removal at latter stages may be attributed to the formation of stable intermediates. At the end of electro-oxidation for four hours, the reduction in COD by electrode B was found to be significantly higher than that of electrode A. As seen from Table 2, the BOD, color and total dissolved solid reduction is also greater for electrode B than electrode A. Electrodes prepared at 450°C and 550°C gave 84% and 96% color removal respectively. COD removal was found to be 68% and 79% for the electrodes prepared at 450°C and 550°C respectively. The efficient electrooxidation performance of electrode A, when compared to that of electrode B can be attributed to the effect of microstructural modifications on the RuO<sub>2</sub> electrocatalytic coating, which is rendered by sintering at 550°C. The smaller grain size and greater porosity of stable anatase RuO<sub>2</sub> coating on the Ti mesh substrate results in the formation of a greater number of active sites for enhanced pharmaceutical effluent electro-oxidation.

### FT-IR Spectral Studies

The FT-IR spectra for untreated and treated pharmaceutical effluent using electrode B were recorded on Thermo Nicolet Nexus 670 FT-IR spectrophotometer in the range between 400 and 4000 cm<sup>-1</sup>. The samples were dispersed in pure KBr crystals to prepare pellets for analysis. From the spectra (Figure 8) it can be concluded that major structural changes might have occurred during the electrochemical oxidation process (electrodes prepared at electrode B). The functional group peaks covering the 700-1800 cm<sup>-1</sup> region show that most of the peaks of raw effluent (8(b)) have disappeared or decreased in intensity in the spectrum of treated effluent (8(a)). Peaks at 3418, 1615, 1513, 1055 and 608 cm<sup>-1</sup> correspond to N-H, C-N and carbonyl groups. The characteristic absorption peaks of alcoholic O-H groups were found at 3418 and 1398 cm<sup>-1</sup>. The cyclic and acyclic ether linkage(C-O-C) absorbs at 1190 and 1118 cm<sup>-1</sup>. After treatment, the intensities of amine

S. no.	Parameter	After electrooxidation (electrode A)	After electrooxidation (electrode B)
1	Color	Pale yellow	Colorless
2	pH	7.8	7.5
3	COD	504 mg/l	320 mg/l
4	BOD	185 mg/l	115 mg/l
5	Total dissolved solids	185 mg/l	163 mg/l

**Table 2:** Physico-chemical characteristics of pharmaceutical effluent after electrooxidation.



and O-H groups got reduced. This is mainly due to the fact that the organics present in pharmaceutical wastewater are converted into other secondary products. The reduction of peak intensity at 1190 and 1118  $\text{cm}^{-1}$  may be due to the breaking up of cyclic ether linkage (C-O-C) and tetra hydropyran and cyclohexane rings are formed. Appearance of new peaks at 2926 and 2854  $\text{cm}^{-1}$  and a low intense peak at 1445  $\text{cm}^{-1}$  proves the formation of cyclohexane and tetra hydropyran ring in effluent. From the results, all characteristic absorption peaks appear reduced in the spectra. This indicates that the organics present in the effluent have converted into some other products such formic, oxalic and acetic acids. Further, these acids may get converted to  $\text{CO}_2$  and water. The observations from FT-IR data point at the efficiency of  $\text{RuO}_2/\text{Ti}$  electrode B, prepared by sintering at  $550^\circ\text{C}$  for electro-oxidation of pharmaceutical effluent.

## Conclusion

This contribution has reported the effect of  $\text{RuO}_2$  microstructure on Ti substrate anodes with respect to efficient electrochemical oxidation of pharmaceutical effluent. Electrodes were prepared by sintering at two different temperatures viz.  $450^\circ\text{C}$  (Electrode A) and  $550^\circ\text{C}$  (Electrode B), and electro-oxidation was carried out at a current density of 3 A/dm<sup>2</sup> for 4 hr. Color removal of 84 % and 96 % were recorded electrodes prepared at  $450^\circ\text{C}$  and  $550^\circ\text{C}$ . COD removal was found to be 68 % and 79 % for the electrodes prepared at  $450^\circ\text{C}$  and  $550^\circ\text{C}$  respectively. Electrode B also exhibits more efficient redox behavior than that of electrode A, as depicted by results from cyclic voltmmetry. The efficient electro-oxidation performance of electrode A, when compared to that of electrode B can be attributed to the effect of microstructural modifications on the  $\text{RuO}_2$  electrocatalytic coating, which is rendered by sintering at  $550^\circ\text{C}$ . This can be construed from the SEM and XRD results provided. The smaller grain size and greater porosity of stable anatase  $\text{RuO}_2$  coating on the Ti mesh substrate results in the formation of a greater number of active sites for enhanced pharmaceutical effluent electro-oxidation. Thus, this contribution reports that preparation of  $\text{RuO}_2/\text{Ti}$  anode by sintering at  $550^\circ\text{C}$  would be an efficient technique for bringing about effective electro-oxidation of pharmaceutical effluent.

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